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THEORETICAL STUDIES OF THE C_4 MOLECULE

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ABSTRACT. Optimized geometries and relative energies for three states
of the C_4 molecule have been obtained from single-reference configura-
tion interaction (SRCI) calculations. The $^1\Sigma_g^+$ acetylenic form corre-
lates with two ground state $^1\Sigma_g^+$ C_2 molecules, from which it can be
formed without activation. The $^1\Sigma_g^+$ state, however, is calculated to
lie approximately 25 kcal above the $^3\Sigma_g^-$ state. At the SRCI level, a
rhombic form is calculated to lie 1.1 kcal below the triplet form;
consideration of the Davidson correction reduces this difference to
0.4 kcal, while more complete basis sets are expected to increase the
difference only by about 0.2 kcal. Consideration of these effects and
difference in zero-point energy leads to a final estimated splitting of
1.2 kcal, favoring the rhombus. To aid the determination of the ground
state, preliminary estimates of the lowest optical transitions were
obtained from SRCI calculations and vibrational frequencies were ob-
tained from SCF calculations. Comparison of the calculated results
with experimentally obtained spectra suggest the possibility that both
the linear triplet and the rhombus may have already been observed.

1.   INTRODUCTION

We have undertaken a theoretical study of small carbon clusters to
determine what role, if any, they may play in soot formation. Theo-
retically, small carbon clusters have been the subject of several
investigations.[1-4] Experimentally, C_2[5], and C_3[6] are well-characterized
and often-observed species in combustion and explosive processes. It

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is also known that carbon in the form of soot is also frequently produced in combustion and explosive processes, usually with deleterious effects. C_4 was studied first because it is a simple dimer of C_2, the most abundant molecular form of carbon. Furthermore, C_4 may have an acetylenic ($^\bullet C \equiv C - C \equiv C^\bullet$, 1) or cummulenic ($^3 : C = C = C = C :$, 2) structure. The relative energies of these forms are important for determining the structure of sp hybridized allotropes of carbon, which may likewise occur in acetylenic ($^\bullet (C \equiv C)_n{}^\bullet$) or cummulenic ($^3 : (C = C)_n :$) forms.

Our aim is to calculate the thermodynamic and kinetic stability of C_4, as well as to calculate spectroscopic constants to aid in the identification and characterization of C_4. Observations attributed to C_4 have been previously reported.[7,8]

Additional interest arises from reports that a rhombic structure (3) is calculated to be the ground state for C_4.[4]

1   2   3
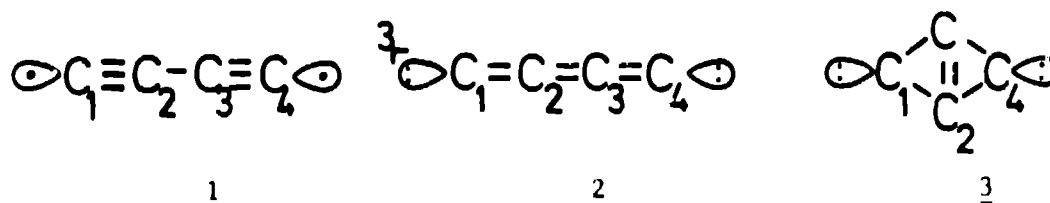
2. METHODS

Calculations were performed with Dunning's double zeta plus polarization basis set,[9] unless otherwise noted. The MOLECULE-SWEDEN codes were used on a Cray computer.[10]

CI calculations for these species included all single and double replacements from the reference function. For the rhombus, the reference function is the closed shell SCF configuration. For the triplet, it is the RHF-SCF configuration; i.e.: $(core)5\sigma_g{}^2 4\sigma_u{}^2 \pi_u{}^4 \pi_g{}^2$. Because of the biradical character of 1, two-configuration SCF optimized orbitals were used in the CI treatment. The reference function for the CI calculations is composed of those configurations from the two-configuration SCF wavefunction; i.e.: $(core)5\sigma_g{}^2 \pi_u{}^4 \pi_g{}^4 4\sigma_u{}^0$ and $4\sigma_u{}^2 \pi_u{}^4 \pi_g{}^4 5\sigma_g{}^0$.

Optimized geometries were obtained from grid searches.

3. RESULTS AND DISCUSSION

3.1 Dimerization of C_2

A series of calculations were performed in which two $^1\Sigma_g^+$ C_2 molecules approached each other along a linear path. The two C_2 internuclear distances were fixed at 1.203 Å. To account properly for the biradical character of the two reactant molecules and the C_4 product, 4 electron in 4 orbital Complete Active Space SCF (CASSCF) calculations were performed at each point along the reaction path. For these calculations, the 3-21G basis set was employed.[11]

The results of these calculations showed that there is no barrier to the formation of $^1\Sigma_g^+$ C_4 along a linear approach of two C_2 molecules and that the reaction is 127 kcal exothermic when calculated in this fashion. These results are in keeping with the biradical character of the C_2 molecules. Thus, 1 represents a kinetically viable intermediate.

3.2 Linear and Rhombic Structures

Results from geometry optimization for 1, 2, and 3 are presented in Table I. For the $^1\Sigma_g^+$ and $^3\Sigma_g^-$ cases, slight deviations from linearity along either of the two bending modes resulted in higher energies. regardless of the level of theory used. For the rhombic case, deviations from planarity resulted also in higher energies at all levels of theory.

The acetylenic nature of 1 is evidenced by the short C_1-C_2 bond length and the longer C_2-C_3 bond length. In comparison, butadiyne has C-C bond lengths of 1.218 and 1.384 Å.[12] A large amount of biradical character is indicated by coefficients of about 0.68 and -0.63 for the two configurations corresponding essentially to doubly occupied in-phase and out-of-phase combinations of sigma orbitals primarily on C_1 and C_4. The equilibrium acetylenic form of C_4 lies energetically above the triplet and rhombic equilibrium forms, as well as several other states; thus, it is only metastable.

The $^3\Sigma_g^-$ form was verified to be stable to bending at the CI level. At the optimized geometry, the coefficient of the reference function in the normalized CI wavefunction is -0.924. This state of C_4 has nearly equal bond lengths characteristic of a cummulene. For example, buta-triene has a C_1-C_2 bond length of 1.318 Å and a C_2-C_3 bond length of 1.283 Å.[13] The similar bond lengths in 2 and butatriene occur because the two unpaired electrons of 2 are in orthogonal orbitals having the same nodal properties as that of the highest doubly occupied pi orbital in butatriene. This trend is general and it is expected that the bond lengths of the $^3\Sigma_g^-$ form of C_n, where n is even, will be very similar to

those of the analogous cummulene.

The rhombic form has been suggested as the ground state for C_4^4. This form is particularly interesting because it possesses a bond between inverted sp^2 centers. Bonds between inverted sp^3 carbons have been previously investigated.[14] At the optimized geometry, the coefficient of the reference function in the normalized CI wavefunction is 0.927. The calculated bond lengths listed in Table I are slightly longer, as would be expected, than those obtained with the 6-31G* basis set of 1.425 and 1.457 for C_1-C_2 and C_2-C_3, respectively. The C_2-C_3 bond undergoes the greater change and its length is not at all characteristic of a typical double bond as it is represented in 3.

Because of the unique bond between inverted carbons, the effect of the inclusion of correlation was further examined. Figure 1 shows a map of the electron density obtained from a CI calculation less that obtained from an SCF calculation. The CI optimized geometry was used for both calculations. Electron density is removed from near the bond mid-points and placed closer to the atoms in the CI calculation. The bond between the inverted carbons as shown on the left in Fig. 1 has two symmetry-related regions along the internuclear axis of increased density between the carbons. Similar features are not observed for bonds along the periphery.

Figure 2 shows density difference maps created by subtracting an electron density distribution obtained from a superposition of sphericalized SCF (double-zeta plus polarization basis) atoms from that of the molecular CI calculation. Deformation density maps were used in a discussion of bonding between inverted sp^3 hybridized carbons.[15] In contrast to the bond between inverted sp^3 carbons, a positive deformation density is found in the bond between inverted sp^2 carbons. Inclusion of CI, it will be recalled, reduces the density at the C_2-C_3 bond midpoint, so this difference is not a result of the CI wavefunctions used in this work. Lone pairs of electrons are apparent at C_1 and C_4. Peaks of about 0.07 e/au^3 are observed near the mid-points of bonds along the periphery. Interestingly, these peaks lie near if not directly on the internuclear axis indicating little if any bent bond character.

The deformation density found in the bonds along the periphery contrasts with that found between the inverted centers. The density deformation at the mid-point of the C_2-C_3 bond is about 0.03 e/au^3 - less than that for the other bonds, even though the $C2$-C_3 bond is represented as being of higher bond order. Displacements from this point along the C_1-C_4 vector result in larger values of the density deformation. Displacements from this point along the C_2-C_3 axis result in lesser values of the density deformation. Inspection of the deformation

density in the plane containing the pi bond reveals electron density has been built-up along the internuclear axis and depleted from the atoms' p orbitals.

3.3 Spectroscopic Data

Calculated vibrational frequencies for the linear triplet and the rhombus are shown in Tables II and III. Results for the linear triplet species were obtained using the UHF method and the 6-31G* basis set. Results for the rhombus were obtained using the RHF method with the DZP basis set. Vibrational frequencies calculated in either fashion are usually about 9-11% too high for stretching modes.[16] Bending modes are usually thought to be more accurate, although the observed low bending frequency for C_3 is overestimated at the level of theory used here.[17]

Weltner observes a 2170 cm^{-1} IR absorption, which was previously assigned by Thompson to the stretching mode of an acetylenic C_4 species. In $\underline{2}$, the calculated frequency for this IR allowed mode of 1740 cm^{-1} seems in good agreement with the essentially cummulenic structure. Indeed, the IR spectrum of butatriene is reported as having absorptions in this region at 1708 and 1610 cm^{-1}; the only higher frequency absorption occurs at 2990 cm^{-1} and is almost certainly a C-H stretch.[18] Thus, it is unlikely that the 2170 cm^{-1} band results from $^3\Sigma_g^-$ C_4. As discussed above though, $\underline{1}$ is a kinetically accessible state, even at the very low frozen rare gas matrix temperatures, and a stretching frequency of 2170 cm^{-1} is qualitatively consistent with the calculated structure.

Low-lying optical transitions from the $^3\Sigma_g^-$ and the ^1A_g rhombus were also calculated and are listed in Table IV. Three levels of theory were used: SCF, SRCI, and the Davidson corrected CI.[19] There are two low-lying transitions for the $^3\Sigma_g^-$. Using Davidson corrected CI energies, the $^3\pi_u$ transition is predicted to lie below the $^3\Sigma_u^-$ transition. The $^3\pi_u$ state may even drop lower at higher levels of theory because of its multi-reference character. On the other hand, the $^3\Sigma_u^-$ state appears to have less multi-reference character.

Weltner observed two UV absorptions in rare gas matricies and assigned them to C_4. These bands were regarded as arising from a vibrational progression of an electronic transition from the $^3\Sigma_g^-$ state. The results in Table IV suggests the possibility that the observed 19569 cm^{-1} (19765 calculated) is the ^1A_g to $^1B_{2u}$ absorption of

the rhombus, while the observed 21659 cm^{-1} (21291 calculated) results from the $^3\Sigma_g^-$ to $^3\Sigma_u^-$ transition. While it would be a fortunate coincidence for the calculations to be of the accuracy implied by the assigned transitions, it does seem quite plausible that the experiment results in more than one C_4 species. This interpretation requires that either or both of two possibilities be true: the rhombus and linear triplet lie extremely close in energy, as the calculations suggest, or that a non-thermodynamic mixture is trapped in the rare gas matrix. The latter could occur because the C_4 is formed from reactions of smaller carbon clusters at 4 to 25 K.

3.4 The Ground State of C_4

As indicated in Table I, at the SRCI level of theory the rhombus is favored by 1.1 kcal. Consideration of the Davidson correction lowers this preference to only 0.4 kcal. The calculated zero-point energies differ by 0.7 kcal, favoring the rhombus again. Inclusion of an extra set of diffuse d orbitals in the basis set followed by a SRCI calculation appears to favor the rhombus very slightly, by about 0.2 kcal. Starting with the 0.4 kcal figure, then adding the 0.2 kcal difference to account for an incomplete basis set and the 0.6 kcal (reduced by ~10% to account for the overestimation of vibrational frequencies at the SCF level) difference in zero-point energies, the rhombus would be favored by 1.2 kcal. This result is close to that of 2.5 kcal obtained from RMP4 calculations.[4] The absolute value of this splitting is not so important as realizing that the two structures are very close in energy.

4. ACKNOWLEDGMENT

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TABLE I. Optimized parameters for some C_4 structures. Results for $^3\Sigma_g^-$ and rhombic C_4 were obtained at the single-reference CI level. Results for the $^1\Sigma_g^+$ structure were obtained using a two-configuration reference function for the CI calculations. See text for details. Bond lengths in Å.

	$^1\Sigma_g^+$	$^3\Sigma_g^-$	Rhombus
$R(C_1-C_2)$	1.213	1.316	!.448
$R(C_2-C_3)$	1.398	1.297	1.500
Rel Energy (kcal)	0.0	-24.7	-25.8

TABLE II. Calculated vibrational frequencies in cm^{-1} and resulting zero-point energy for $^3\Sigma_g^-$ C_4. The 6-31G* geometry was used.

Mode	Frequency
πu	209.3
πg	407.7
σg	1021.5
σu	1740.5
σg	2345.0
ZPE	9.1 kcal

TABLE III. Calculated vibrational frequencies in cm^{-1} and resulting zero-point energy for rhombc C_4. The DZP SCF optimized geometry was used.

Mode	Frequency
b_{3u}	345.2
b_{1u}	443.5
a_g	1061.3
b_{1g}	1086.7
a_g	1419.2
b_{2u}	1541.3
ZPE	8.4 kcal

TABLE IV. Low-lying optically allowed transitions in cm^{-1} at various levels of theory.

	SCF	SRCI	Davidson
From $^3\Sigma_g^-$ to:			
$^3\Pi_u$	30,556	20,049	15,488
$^3\Sigma_u^-$	14,729	19,797	21,291
From ^1A_g to:			
$^1B_{2u}$	27,317	21,592	19,765

RHO(CI) — RHO(SCF)

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RHO(CI) — RHO(SCF)

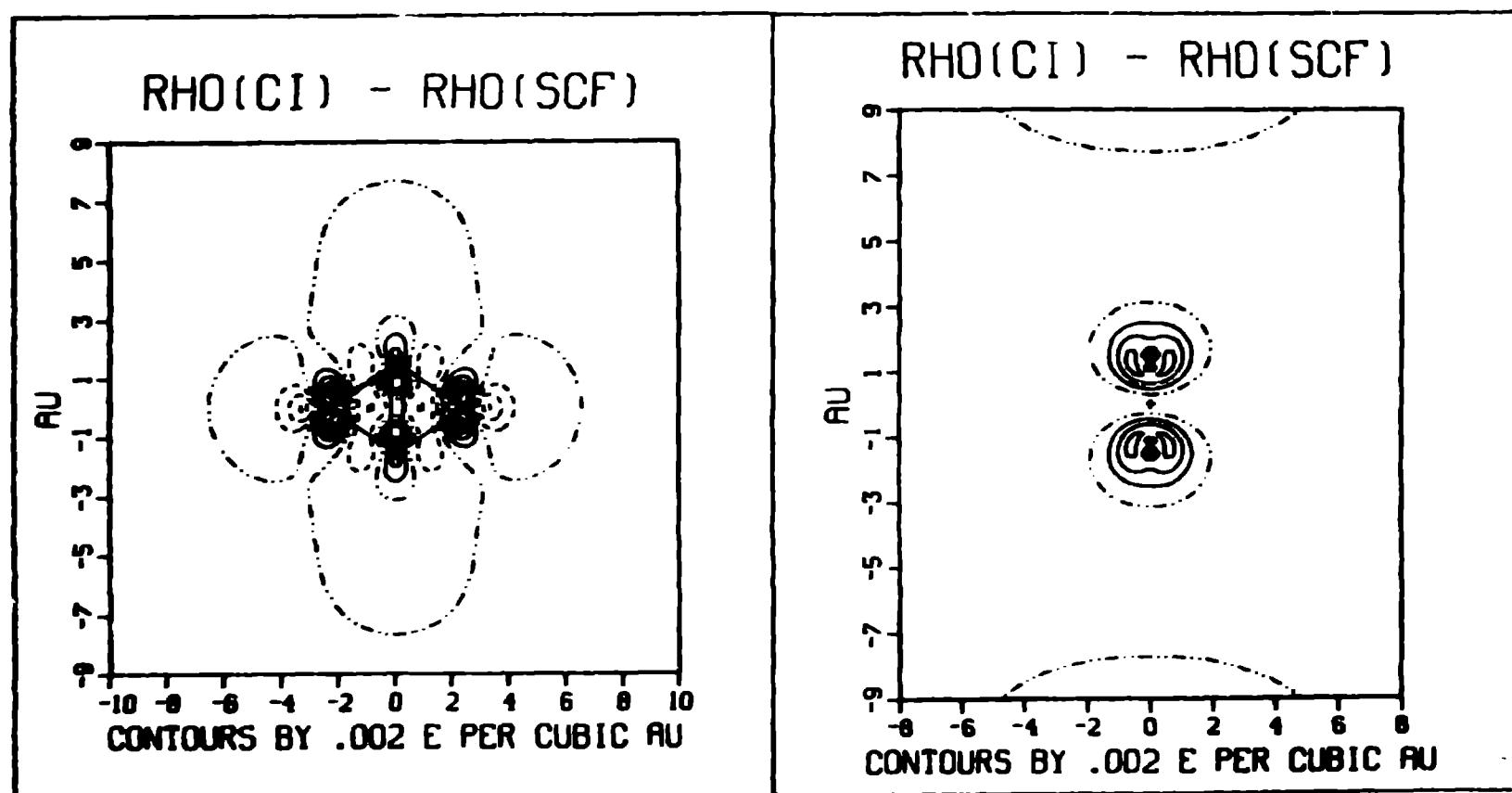CONTOURS BY .002 E PER CUBIC AU

Figure 1. Electron density distribution obtained from CI calculations less that obtained by SCF calculations. Illustrated planes are in the plane of the molecule (left) and in the perpendicular plane containing the pi bond. Solid lines represent positive values, dashed lines represent negative values, and the combination dash-dot-dot lines represent zero as a value. Atom positions in the illustrated planes are indicated by a dark circle (●), while projections of atoms not in the plane are indicated with a plus (+).
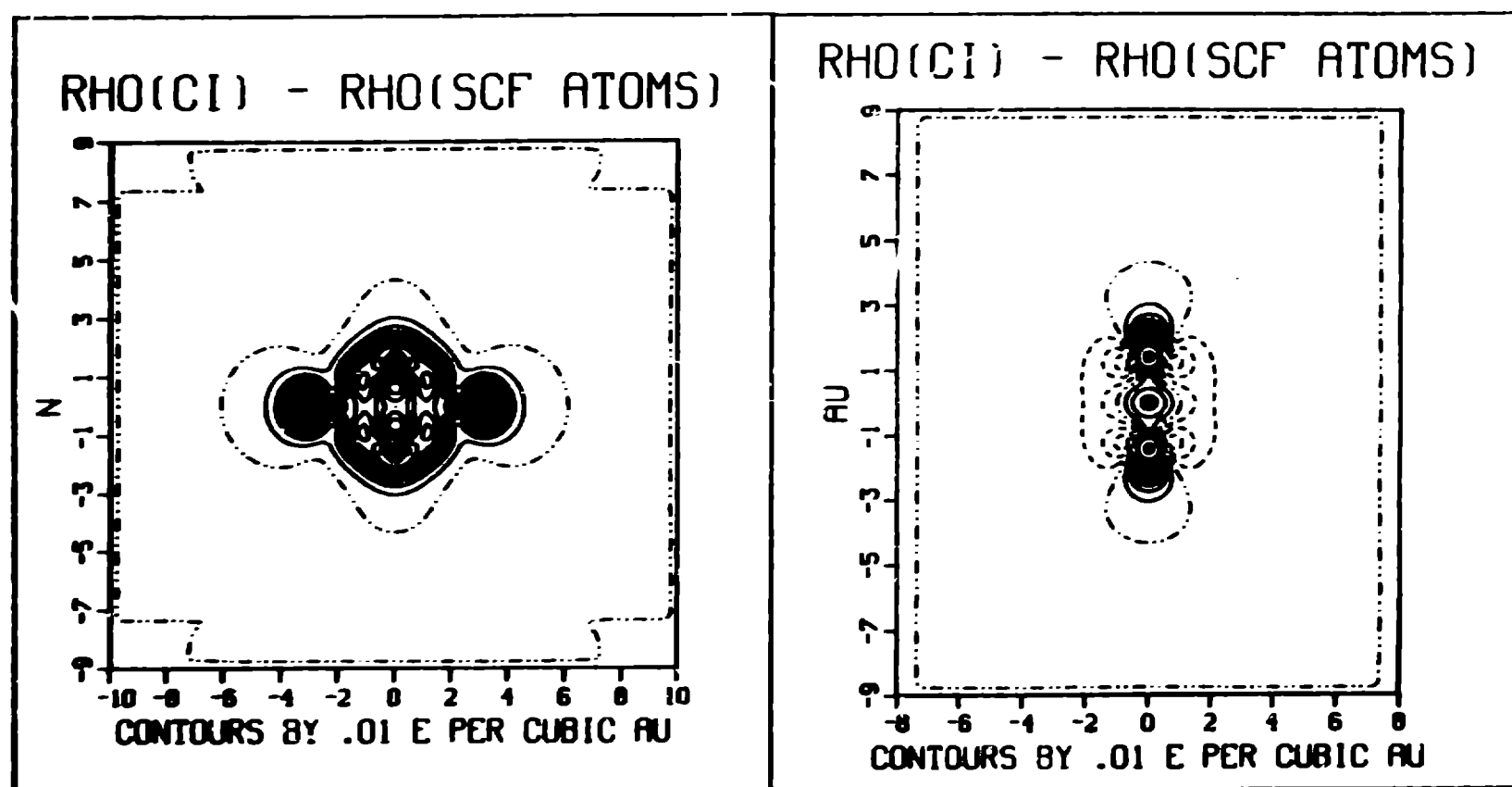
Figure 2. Electron density distribution obtained from a CI calculation less that obtained from a superposition of spherical atoms from SCF calculations. Plots are presented as in Figure. 1.